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# TRANSLATION

CERTAIN CHARACTERISTICS OF WELDING  
TITANIUM UNDER FLUX

By

S. M. Gurevich

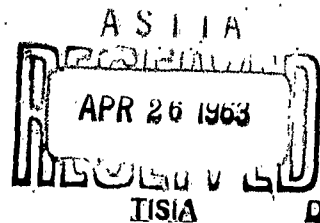
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## UNEDITED ROUGH DRAFT TRANSLATION

CERTAIN CHARACTERISTICS OF WELDING TITANIUM UNDER  
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BY: S. M. Gurevich

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## Certain Characteristics of Welding Titanium under Flux

by

S. M. Gurevich

Explained are metallurgical and technological characteristics of automatic welding of titanium under flux. It is shown, that during flux-slag reaction with the metal are possible interchange reactions of titanium and its oxides with components of oxygen-less flux.

Discussed are the characteristics of melting the metal and the thermal cycle in the near-seam zone during the welding of titanium.

### 1. Reactivity of titanium and the requirements for the flux for its welding

Titanium at high temperatures react energetically with atmospheric oxygen and nitrogen. Oxidation of titanium begins at a temperature of about 600°C. Up to this temperature the metal is protected by an oxide film, which firmly adheres to the surface of titanium, since it has a structure, similar to metal. The most intensive solution of the oxide film in titanium, is accompanied by the most intensive diffusion of the oxygen in the interior of the metal, and it begins at a temperature of about 850°C. Solubility of oxygen in titanium reaches 30 atm% [3]. V.I. Arkharov and G.P. Luchkin [4] established that the nitrogen existing in the air speeds up the oxidation of titanium.

The reaction of titanium oxidation follows at maximum rate in comparison with its reaction with other gases. And so, the rate of titanium/oxygen reaction is 50 times greater than with nitrogen [5]. The greater affinity of titanium to oxygen, than to nitrogen, is confirmed also by calculated data, given in form of graphs in fig.1.

The graphs show a change in free energy of titanium oxide and nitride formation in dependence upon temperature by reactions, which in connection with the calculation per 1 g-a of titanium are considered by us in the following manner:



In fig.1 are also shown for comparison graphs for the change of free energy of reaction of 1 g-a of iron in solid and liquid states with oxygen and nitrogen.

It is evident from the graphs, that the activity of titanium during reaction with oxygen and nitrogen is considerably higher than the activity with these gases of iron, the welding of alloys of which has been well investigated. The graphs also show that in this process is preferably formed titanium oxide, because the absolute values of free reaction energy (1) are greater than the values of free reaction energy (2). But the negative values of free reaction energy of titanium with nitrogen are also high and indicate greater reactivity of the metal with this gas.

The titanium/nitrogen reaction products - nitrides dissolve easily in metal. A sharp rise in the rate of reaction of titanium with nitrogen is observed at temperatures of over 600°C.

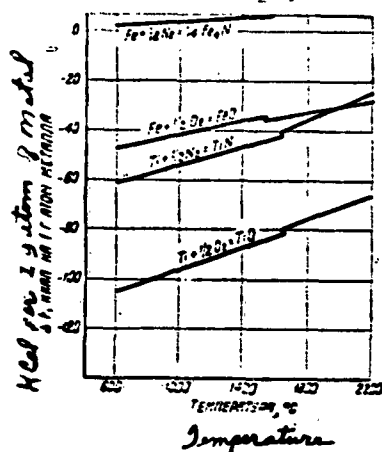


Fig.1. Free energy of formation of titanium and iron oxides and nitrides

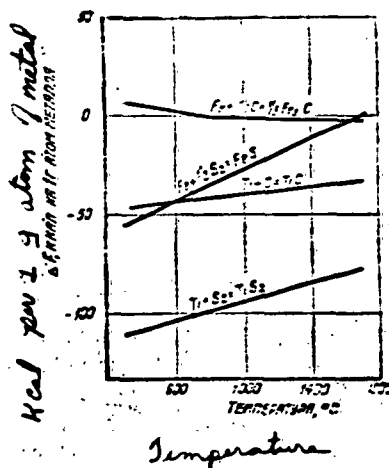


Fig.2. Free energy of formation of titanium carbides and sulfides.

is the  
Very high activity of titanium with respect to hydrogen. Solubility of hydrogen in titanium reaches 33 atm% (atomic percentages) [6] and exceeds by thousands and tens of thousands of times the solubility of hydrogen in iron.

Titanium is highly active during reactions with sulfur and phosphorus (over 1000°C) as result of which are formed sulfides and phosphides. It is also capable of directly combining itself with carbon and silicon with the formation of carbides and silicides. Because of low carbon solubility in titanium the content of several tenths of a percentage of carbon leads to the formation of carbide and to brittleness of the metal.

The results of calculating the values of free energy of formation of titanium and iron carbides and sulfides, given in fig. 2, in form of graphs, show, that the activity of titanium with respect to carbon and sulfur considerably exceeds the activity of iron to these elements.

The brief description of the reactivity of titanium given above shows, that the flux for its welding should be confronted with higher requirements.

It is known, that flux-slag in the process of automatic welding of steel, do well protect the seam metal against the harmful effect of atmospheric gases. In the case of welding titanium such an insulation of the seam against air is necessary, but insufficient. An obligatory condition for the obtainment of a qualitative seam is the absence of the oxidizing effect of flux on the metal. It is also important, that the flux should protect seams against hydrogen saturation and it should not contaminate it by harmful admixtures - carbon, sulfur and phosphorus.

The high melting point of titanium brings forth the need for high meltability of the flux. Finally, as any other welding flux, flux for titanium should assure a stable welding process, excellent formation of seams, absence in the seam of defects - pores, slag inclusions, cracks etc.

Existing fluxes for steel and a number of non-ferrous metals and alloys (e.g. aluminum alloys) are unsuitable for welding titanium. They either contaminate the

metal of the seam with harmful admixtures, first of all oxygen, or they extremely low-melting.

It is prohibited to introduce into the composition fluxes for titanium silicon, manganese oxides and even such highly stable oxides as aluminum, zirconium and titanium oxides.

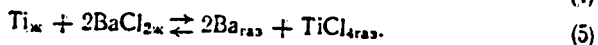
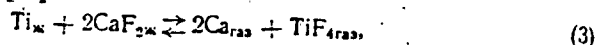
Positive results can be obtained only by using for titanium fluxes, containing no oxides. Such oxygen-free fluxes are obtained by melting most high melting fluorides and chlorides of alkali and alkali-earth metals.

## 2. Metallurgical Characteristics of Welding Titanium under Flux

Include in the number of important metallurgical characteristics of welding Ti under flux is also the reaction of the metal of the welding bath with flux-slag. Thermodynamic calculations, as well as certain direct investigations show that two types of reactions are possible: a) reaction of Ti with flux components and b) reaction of titanium oxides with the flux.

As examples are given below calculations of free reaction energy values of both types for three component systems consisting of most high melting fluoride and chloride of alkali-earth metals-CaF<sub>2</sub> and BaCl<sub>2</sub> and fluoride of alkali metal - NaF.

Basic reactions during the interaction of liquid titanium with the mentioned components can be written in following form:



To calculate the free energy of these reactions were calculated the values of heats of formation ( $\Delta H_{298}^0$ ) and entropy ( $S_{298}^0$ ) of liquid titanium at standard conditions.

The calculation of heat of formation of liquid titanium at standard temperature of 298°K is done in the following manner: solid titanium is heated to the point of melting-melting-hypothetical quenching of liquid Ti to a temperature of 298°K. When calculating were accepted the following thermophysical constant of titanium:



melting point 1660°C [7], latent temperature of formation 4500 cal/mol [8].

Specific heat of solid titanium was calculated by equation:  $C_p = 5.25 + 2.52 \cdot 10^{-3} T$  cal/mol-degree (6) [8].

Specific heat of liquid titanium was accepted as equalling 8 cal/mol-degree [9].

A similar calculation for liquid titanium gives

$$\Delta H_{298}^0 \approx 3670 \text{ cal/mol}$$

The entropy of liquid titanium  $S_{298}^0$  will be calculated by an analogous cycle:

1) entropy of solid titanium 7.3 cal/mol-degree [8];

2) rise in entropy at a rise in temperature to the melting point of Ti 1660°C (1933°K) is determined by equation:

$$\Delta S_1 = \int_{T_1}^{T_2} C_p \frac{dT}{T} = \int_{298}^{1933} (5.25 + 2.52 \cdot 10^{-3} T) \frac{dT}{T} = 13.93 \text{ cal/mol-deg} \quad 6a$$

3) an increase in entropy during the melting of titanium

$$\Delta S_2 = \frac{4500}{1933} = 2.33 \text{ cal/n-deg} \quad 6b$$

4) change in entropy under conditions of quenching liquid titanium to standard temperature

$$\Delta S_3 = \int_{T_1}^{T_2} C_p \frac{dT}{T} = \int_{1933}^{298} 8 \frac{dT}{T} = -14.95 \text{ cal/mol-deg} \quad 6c$$

The entropy of liquid titanium at standard conditions will be

$$(S_{298}^0)_\text{Ti} = (S_{298}^0)_\text{Ti} + \Delta S_1 + \Delta S_2 + \Delta S_3 = 7.3 + 13.93 + 2.33 - 14.95 = 8.61 \text{ cal/mol-deg} \quad 6d$$

Basic data for the calculation of thermal constants of other liquid substances, participating in the reactions (3), (4) and (5), were thermophysical constants for solid substances which were used by [8,10]. Calculations were made in accordance with the cycle, analogous to the one described above.

The value  $\Delta H_{298}^0$  for  $\text{TiF}_4$  was accepted in conformity with experimental data of [11] - 19 ev. To transpose  $\Delta H_{298}^0$  into kilo-calories was accepted the coefficient 23,066 [10]. The entropy of gaseous  $\text{TiF}_4$  at standard conditions was found from equation, valid for polyatomic gases [8].

$$S_{298}^0 = 39.0 + 0.34M - 6.2 \cdot 10^{-4} M^2, \quad (7)$$

where M - molecular weight.

Thermal constants of the substances, participating in reactions (3), (4) and (5) are listed in table 1.

Table 1. Thermal constants of substances, participating in reactions (3), (4) and (5)

Substance	$\Delta H_{298}$ cal/mol	$S_{298}^0$ cal/mol.deg	Source
Ti <sub>2</sub> <i>liq.</i>	3670	8.61	Calculation
CaF <sub>2</sub> <i>liq.</i>	-277030	27.51	ditto
Ca <sub>2</sub> <i>gas</i>	42600	37.	[10]
TiF <sub>4</sub> <i>gas</i>	-438000	71.7	[11], [9]
NaF <sub>2</sub> <i>liq.</i>	-104400	18.6	calculation
Na <sub>2</sub> <i>gas</i>	25950	36.72	[10]
BaCl <sub>2</sub> <i>liq.</i>	-200000	34.6	calculation
Ba <sub>2</sub> <i>gas</i>	490000	40.67	[10]
TiCl <sub>4</sub> <i>gas</i>	-180500	84.4	[10]

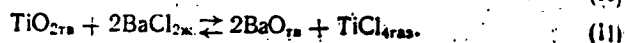
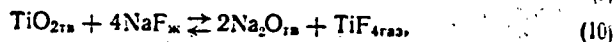
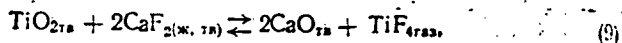
Substituting the thermal constants in equation of free reaction energy

$$\Delta F = \Delta H - T\Delta S,$$

we will obtain values, given in fig. 3 in form of graphs. It is evident from this drawing, that titanium should not react with calcium fluoride and the more so with barium chloride. But the reaction of titanium with sodium fluoride should be very intensive. This is indicated by the greater negative values of free reaction energy [1].

In this way, thermodynamic calculations show the possibility of recovering sodium from sodium fluoride by titanium. This also, apparently, explains the modifying effect which flux is exerting on the titanium seam, a flux containing sodium fluoride [1].

Reactions of second type at temperatures of over 1000°C can be presented in following form:



Possible are also reactions of the type



However calculations show, that they do not bring in any principal changes into the thermodynamic characteristics of titanium oxide reactions with fluorides and

chlorides. Consequently to evaluate the possibility of the reaction taking place it is sufficient to compare monotypical reactions (9), (10) and (11).

In table 2 are given thermal constants of substances, participating in these reactions.

Table 2. Thermal constants of substances, participating in reactions (9), (10) and (11)

1 Substance	2. $\Delta H_{298}^0$ cal/mol	3. $S_{298}^0$ cal/mol.deg	4. Source
$TiO_2$	-225500	12.0	[8]
$CaF_2$	-290300	16.45	[8]
$CaO$	-151900	9.5	[8]
$Na_2O$	-100400	17.0	[8]
$BaO$	-133400	16.8	[12]

Results of calculating free energy of reaction (9), (10) and (11) are given in fig. 4.

Graphs show, that at high temperatures (over 1000 - 1100°C) are possible titanium oxide reactions with fluorides and no reaction with chloride. The correctness of the calculation is confirmed by data from [13], in which are given certain results of calculations of  $TiO_2$  reaction with fluorides. It should be mentioned, that the solubility of titanium oxides in fluorides also exceeds their solubility in chlorides [14, 15].

It is evident from thermodynamic calculations, that the components of  $CaF_2$  and NaF flux may enter into reaction with titanium oxide. This property of the flux, together with its ability to dissolve titanium oxides, appears to be highly valuable; it, apparently, plays an important role in protecting the metal of the seam during the welding against oxygen contamination.

The dissolving of titanium oxides in flux is indicated by the dark-grayish color of the solidified slag crust, characteristic for lower oxides of titanium. Chemical analysis of the slag crust enabled to establish the presence in it of alkali oxides, which indicate that the above mentioned interchange reactions between flux-slag and titanium oxide has actually taken place.

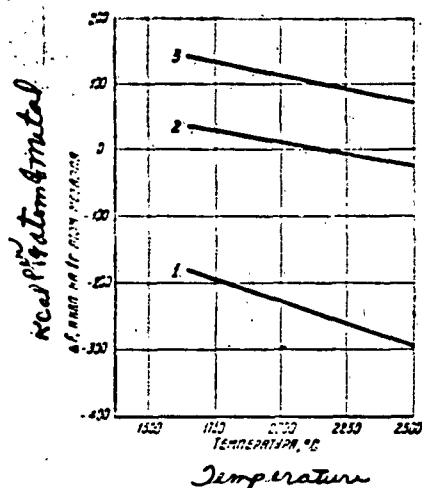


Fig. 3. Free energy of titanium reaction with NaF, CaF<sub>2</sub> and BaCl<sub>2</sub>

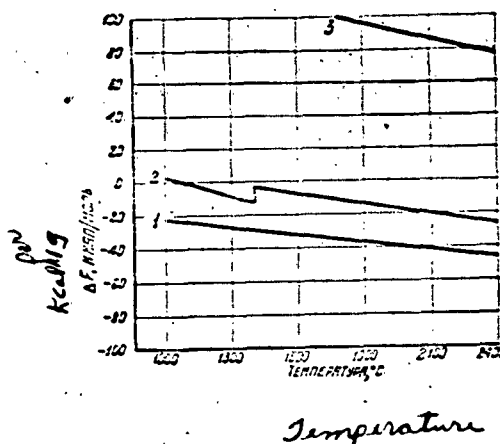
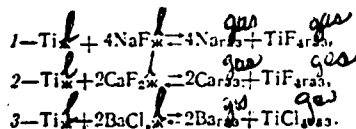
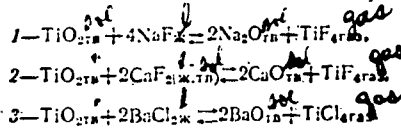


Fig. 4. Free energy of titanium oxide reaction with NaF, CaF<sub>2</sub> and BaCl<sub>2</sub>



The nature of the discussed flux-slag reactions with the metal allows to make the following conclusions:

a) from the viewpoint of most complete metallurgical reaction between flux and Ti and its oxides in the composition of the flux it is desired to have a maximum amount of fluorides and a minimum of chlorides;

b) of the fluorides in the role of flux components are most suitable the ones, which together with the high melting point possess maximum ability to react with titanium oxides.

But investigations showed, that flux, consisting of fluorides only, does not possess the required technological qualities. Better results are obtained by substituting part of the fluorides with chlorides.

As to protection of seam metal against contamination with nitrogen and hydrogen then as shown by numerous investigations, flux in the process of welding reliably

isolates the welding bath and remaining parts of the seam and near seam zone against harmful effect of atmospheric gases. This is indicated by results of gas analyzing seam metal of technical titanium with a thickness of 2.0 and 4.5 mm, listed in table 3. In the table for the purpose of comparing is given the content of basic admixtures of the welded metal.

Table 3. Content of basic admixtures in welded seams of techn. titanium made under Al-Ti flux  
Electrode of the very same composition as basic metal

Thickness of metal, mm	Metal	Content of admixtures, weight %			
		Nitrogen	Oxygen	Hydrogen	Carbon
2.0	Basic seam	0.029	0.175	0.019	0.07
		0.025	0.175	0.020	0.05
4.5	Basic seam	0.057	0.078	0.014	0.06
		0.030	0.077	0.012	0.04

The amounts of hydrogen in the seam metal, as indicated in table 3, can be obtained only when using dry granulation flux. Use of wet granulation flux leads to a noticeable rise in hydrogen content in the seam (increase by 30-40%).

### 3. Technological Characteristics of Welding Titanium under Flux

#### a) Characteristics of thermal cycle in near seam zone and meltings of basic metal.

Titanium has low heat conductivity, which is almost 4 times lower, than in steel. Consequently, when welding titanium there is less energy loss, than during the welding of steel. In addition, concentrated welding heating leads to a more considerable temperature gradient, with which the growth of internal stresses is connected. This must be taken into consideration when selecting optimum conditions for welding titanium structures.

The low heat conductivity of titanium is reflected also on the thermal cycle of the seam metal and the near seam zone.

We will make a comparative evaluation of thermal cycles in the near seam zone for titanium and steel. Since in the near seam zone of titanium and its alloys do occur martensite conversions, it is of interest to make such a comparison with alloyed

hardening steel, for which the conversion kinetics in the zone is also martensitic.

We shall determine by calculation what distinguishes the rates of quenching in the near seam zone of titanium and steel. We adopt a most simple case of calculation - building up of a roller on a thick sheet. The instantaneous rate of quenching for this case is determined from equation [19]:

$$\omega = \frac{2\pi\lambda(T-T_0)^2}{q/v}, \quad (13)$$

where  $\lambda$  - coefficient of heat conduction, cal/cm.sec, °C;  $T$  - instantaneous temperature in the given point of near seam zone, °C;  $T_0$  - initial temperature of the metal, °C;  $q$  - effective thermal force of the arc;  $v$  - rate of welding.

At various losses of the driving energy during welding, i.e. at identical  $q$  and  $v$  values, the ratio of the quenching rate for steel  $\omega_{st}$  to the rate of quenching of titanium  $\omega_T$  can be determined from expression

$$\frac{\omega_{st}}{\omega_T} = \frac{\lambda_{st}(T-T_0)^2}{\lambda_T(T-T_0)^2} \quad (14)$$

We accept the value of the heat conduction coefficient: for alloyed structural steel  $\lambda_{st} = 0.10$  cal/cm.sec °C [20], for technical titanium  $\lambda_T = 0.033$  cal/cm.sec °C [21].

We will find the ratio of quenching rates for two temperatures: 1) close to solidus and 2) near the point of martensite conversion.

We assume that  $T_0 = 20^\circ\text{C}$ , for steel  $T_{\text{melt}} = 1500^\circ\text{C}$ , for titanium  $T_{\text{melt}} = 1660^\circ\text{C}$ . therefore the first calculated temperature

$$\frac{\omega_{st}}{\omega_T} = \frac{0.10 \cdot 1480^2}{0.033 \cdot 1640^2} \approx 2.8. \quad 14a$$

Having accepted approximately for alloyed steel an initial martensite conversion temperature  $T_M = 400^\circ\text{C}$  and the very same temperature for titanium alloys [22] we will obtain for the second calculated temperature

$$\frac{\omega_{st}}{\omega_T} = \frac{0.10 \cdot 380^2}{0.033 \cdot 380^2} \approx 3.0. \quad 14b$$

In this way, the rate of quenching in the near seam zone of titanium, at other conditions remaining equal, is approximately 3 times lower, than in steel.

Thermal calculations by N.N. Rykalin show, that approximately, by as many times

for titanium, as compared with steel, is increased also the time the metal of the near seam zone remains in the zone of high temperatures.

## GRAPHIC NOT REPRODUCIBLE

Fig.5. Single passage butt seam of technical titanium with  
a thickness of 10 mm X 1.8

Slowed down quenching of near seam zone, particularly in the range of martensite conversion temperatures, has a favorable effect on the final properties of this structural section of welded joint, because it leads to a reduction in volumetric structural stresses.

As to the duration of metal exposure at high temperatures and grain growth in the overheated section of the near seam zone connected with it, then this factor must be taken into consideration when selecting optimum welding conditions of various types of joints. Titanium is capable of grain growth when heated to above critical temperatures, i.e. in the zone of  $\beta$ -phase. The growth of grain in the near seam zone of titanium may lead to a reduction in strength and plasticity of welded joint [16]. It is therefore necessary to avoid the use of conditions with extremely high losses of driving energy. (linear energy).

The selection of conditions for welding titanium under flux with minimum values of linear energy is facilitated by the fact, that thanks to specific physical properties of the metal it is possible to obtain the necessary melting depth at relatively low welding currents, and also thanks to the possibility of welding at greater speed [2].

D.M. Rabkin [17] showed that the depth of melting at given welding current depends basically upon the specific weight of welded metal and is not connected with its

heat conductivity.

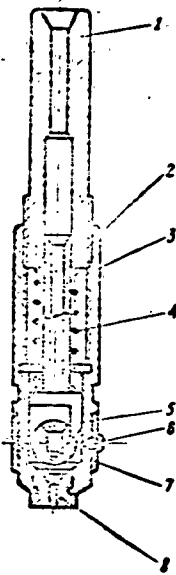


Fig.6. Spout for automatic welding with titanium is required a current approximately titanium electrode wire.

1-holder; 2-body; 3-push rod; 4-spring; 5-clamping washer; 6-fixing screw; 7-ring 8-tip.

Thanks to this during arc welding with uniform welding currents the depth of melting aluminum is approximately three times greater than that of steel, which corresponds to the ratio of specific weights of these metals [17]. Conclusions made by [17] are fully confirmed also for the case of titanium welding. And so at a single pass welding under flux of 10 mm thick sheet steel is necessary a welding current of 750 amp [18]. A titanium butt seam of very same thickness can be welded at a current of 450 amp. (fig.5). In this for

1.7 times lower, than for steel of very same thickness. The specific weight of titanium is also 1.75 times lower than that of steel.

But the heat conductivity of titanium, as we have shown above, is approximately 4 times lower than in steel.

#### b) Need of Welding with Small overhang of the electrode

Some technological features of welding titanium under flux are connected with the use of titanium electrode wire. In this case the necessary condition for a stable welding process and good formation of seam is to provide a constant small overhang of the electrode. Titanium possesses higher electro-resistance, exceeding this characteristic

for iron by almost 6 times. Consequently a greater overhang at current densities characteristic for automatic welding under flux (tens of amperes per square millimeter), leads to overheating the electrode tip and disruption of welding stability. In addition, the heating of the electrode, going into the zone of welding, to temperatures



of over 400-500° is undesirable, because the filler metal becomes contaminated with gases. Even a small change in the overhang in the process of welding (e.g. as result of absence of constant contact in the spout) causes noticeable arc voltage fluctuations and reduce the quality of seam formation. In this case seam defects may appear in form of undercuts.

Optimum overhang values for electrode titanium wire of various diameter are given in table 4.

To weld with an electrode titanium wire of small diameter - 1.2 - 2.5 mm the Ye.O. Patton Electrowelding Inst. at the Academy of Sciences Ukr-SSR developed a tubular spout of special construction (fig.6).

The feature of the spout is, that it reliably assures overhang constancy. This is attained by constantly adjusting the electrode wire to the copper tip of spout 8 with the aid of spring 4, pusher rod 3 and clamping disk 5/.

Table 4. Optimum overhangs of electrode titanium wire

Diameter of electrode wire, mm	1.2 - 1.5	1.5 - 2.5	2.5 - 3.0	3.0 - 4.0	4.0 - 5.0
Overhang, mm	12 - 13	13 - 14	14 - 16	16 - 18	18 - 22

#### c) Protecting Reverse Side of Seam with the Aid of Flux

As is known, an obligatory condition for the obtainment of a qualitative titanium seam is protection against the harmful effect of air not only of the welding bath, but also all sections of the metal, the heating of which reached in the process of welding temperature of 400-500°C. In the practice of welding titanium details are known cases, where even with good protection of the welding zone low quality of the welded joint was obtained because of insufficient insulation of the reverse side (root) of seam from the air.

At present time are applied the following methods of protecting the reverse side of the seam :

- 1) close adherence of welded edges to steel, copper or aluminum backing;

2) using backings with holes or made of porous materials (e.g. porous bronze), through which inert gas is fed;

3) passing of inert gas through the interior of welded vessel.

The first and second methods are applicable only in cases when the reverse side of the seam is accessible for placing the backings. The third method has certain limitations. Consequently, the problem of protecting the root of seams, for which the placing of backings on the reverse side is difficult or impossible, remains so far unsolved (seams of curvilinear configuration, jointing of details under acute angle etc.).

The development of technology for welding titanium under flux gave a new way for solving this problem. It was found, that reliable protection of the reverse side of a titanium seam can be obtained by employing the practically known method of welding steel - flux padding. Good results for titanium were obtained by using fine AN-TI flux as a padding.

Investigations have shown, that single pass welded joints of 4-10 mm thick technical titanium, made under AN-TI flux on a flux padding, have fine plasticity and tenacity. The content of harmful admixtures in the seam metal does not exceed their amount in seams, welded under flux and protected on the reverse side by a copper backing with argon blasting.

The retention of the flux to the welded edges can be realized by various methods: by placing the object on a flux padding, fluxbelt backing etc. In difficultly accessible places good results are yielded by gluing on to the welded metal from the side of seam root special pockets of dense fabric, in which the flux dust (AN-TI flux) (siftings from the grinding of flux) are accumulated.

#### Conclusions

1. Flux for welding titanium as result of its specific physico-chemical properties should be oxygen-free and have a sufficiently high melting point.

2. One of the important metallurgical features of welding titanium under flux is the

reaction between flux-slag and the metal.

As result of this reaction are possible the recovery of sodium from sodium fluoride and interchange reactions between titanium oxide and certain components of the flux, mainly fluorides.

3. Thanks to the low specific weight the melting of titanium, at identical welding conditions, is 1.5 to 2 times greater than in steel. As result of low heat conductivity the welded thermal cycle of the seam and near seam zone for titanium, in comparison with steel, differs by reduced (2-3 times) rates of quenching and increase in time the seam metal and near seam zone are exposed to higher temperatures.

4. Due to the greater electric resistance of titanium electrode wire the welding can be done with the use of small electrode overhangs. The tubular spout of new construction allows to weld with titanium wire of small diameter with the assurance of low overhang.

5. The effective method of protecting the reverse side of single pass titanium seams is the use of flux padding.

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